RESEARCH ARTICLE | FEBRUARY 05 2019

# Addition effect of aliphatic monools and diols on the conductivity enhancement of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) FREE

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*AIP Conf. Proc.* 2065, 020004 (2019)
https://doi.org/10.1063/1.5088254

# Addition effect of aliphatic monools and diols on the conductivity enhancement of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS)

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**Abstract.** The study was made of the addition effect of aliphatic monool and diol compounds (alcohols and glycols) on the conductivity enhancement of PEDOT:PSS films prepared from the aqueous coating mixture. This study made it clear that, 1)there is a large difference in conductivity enhancement ability between monools and diols, 2)the addition of monools have no effect on the conductivity enhancement of PEDOT:PSS films, 3) the addition of diols enhanced the conductivity of PEDOT:PSS films and their conductivity enhancement degree was dependent on the species (chemical structure) of diols, where 1,4-BD showed the highest conductivity enhancement effect among the diols, 4)there is good relationship between the SP values of diols and their conductivity enhancement ability and the diols with the SP values close to PEDOT (10.4) have higher conductivity enhancement ability, 5)diol addition effect was possibly attributable to its good solubility to PEDOT:PSS molecules judging from the SP values.

**Keywords:** PEDOT:PSS, secondary dopant, conductivity enhancement, alcohol, diol, glycol, solubility parameter
**PACS:** 82.35.Cd Conducting polymers

## INTRODUCTION

Indium tin oxide (ITO) used as a transparent conductive material involves some problems such as poor mechanical flexibility, indium scarcity and high production cost. Many researchers have been studying new transparent conductive materials such as poly(3,4-ethylenedioxythiophene) (PEDOT:PSS), silver (Ag) nanoparticles, and nano-carbons such as carbon nanotube (CNT) and graphene as a substituent for ITO. PEDOT:PSS has been attracting considerable attention, since its thin film exhibits a high conductivity and transparency, but it has not conductivity and transparency enough to be replaced for ITO when it is coated as a thin film. Therefore, lots of secondary dopants such as ethylene glycol (EG) and dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) have been proposed and applied to PEDOT:PSS for the conductivity enhancement[1-4]. EG has an excellent conductivity enhancement ability, while methanol (MeOH) has no ability. The reason why there is large difference in the conductivity enhancement ability between EG and MeOH is not made clear. The authors have been studying the effect of organic compounds with hydroxyl groups such as monools (alcohols) and diols (glycols) on the conductivity of PEDOT:PSS and their conductivity enhancement mechanism. In this paper the addition effect of aliphatic monools and diols on the conductivity enhancement and its probable action mechanism in this conference will be discussed.

*Proceedings of PPS-34*
AIP Conf. Proc. 2065, 020004-1–020004-5; https://doi.org/10.1063/1.5088254
Published by AIP Publishing. 978-0-7354-1793-9/$30.00

## EXPERIMENTAL

### Materials and regents

PEDOT:PSS aqueous solution was purchased from Sigma Aldrich company (now Merck company). Its concentration was 1.3% by weight, and the weight ratios of PEDOT and PSS in PEDOT:PSS were 0.5 wt.% and 0.8 wt.%, respectively. Commercial grade of aliphatic monools (methanol(MeOH), ethanol(EtOH), 1-propanol(1-PrOH), 2-propanol(2-PrOH), 1-buthanol(1-BuOH), 2-butahnol(2-BuOH)) and glycols (ethylene glycol(EG), diethylene glycol(DEG), triethylene glycol(TriEG), tetratethylene glycol(TetraEG), 1,3-propanediol(1,3-PG), propylene glycol(PG), dipropylene glycol(DPG), 1,4-butandiol(1,4-BG)) were used without further purification. The solubility parameters (SP) of monools and diols were based on the reference[5,6].

### Preparation of PEDOT:PSS films treated with monools and diols

PEDOT:PSS films were prepared by coating the mixture of PEDOT:PSS aqueous solution (1.3wt%) mixed with aqueous monools (or diols) solution (1.0wt%) with the certain ratio of monools (or diols) to PEDOT:PSS (0.10, 0.25, 0.50, 1.0, 2.0, 4.0) on the commercial glass substrate (2.0cm×5.0cm×1.0mm(thickness)) for an optical microscope and drying the coating layer on the hot plate at 70℃ for 0.5 hr and heat-treated at the temperature of 120℃ for 0.5hr and 170℃ for 0.5hr. The thickness of the dried PEDOT:PSS solid films was controlled to be approximately 10μm.

### Measurement of surface resistivity (Rs) of PEDOT:PSS films

The Rs values of the PEDOT:PSS films formed on the glass plate were measured by the four-point probe device Loresta-GP (MCP-T610, DIA INSTUMENTs co. ltd.) or Model152 (Treck Japan co. ltd.).



## RESULTS AND DISCUSSION

### Addition effect of monools on the conductivity of PEDOT:PSS films

Fig.1 shows the addition effect of monools on the Rs values of PEDOT:PSS films and their Rs values after the heat treatment effect at 120℃ and 170℃. The Rs values of PEDOT:PSS films increased with the increase of monools. The addition of monools had no effect on the conductivity enhancement of the PEDOT:PSS films. Okuzaki[1,2] also disclosed 1,2-PrOH had no effect on the conductivity of PEDOT:PSS films in the similar mixing method. On the other hand, Yijie Xia et al[7]. reported that PEDOT:PSS solid films which was treated with solvents such as methanol (MeOH), ethanol (EtOH) and isopropanol (1,2-PrOH) by dropping method showed lower resistivity (higher conductivity). There is a large difference in the effect of solvent on the conductivity enhancement of PEDOT:PSS films between the mixing method and the dropping method. In the case of the dropping method the excess of PSS is removed from the surface of PEDOT:PSS film by the pure solvent, which may be caused by dissolution of PSS by it. In the case of the mixing method studied here, the monools stay with the PEDOT:PSS aqueous solution and monools are removed from its aqueous solution at the heat-treatment temperature of over 120℃, since boiling points of monools are lower than 100℃ except 1-BuOH. That is to say, the second dopant effect of monools is not expected in the mixing method, since dissolution ability of monools to PEDOT:PSS is almost controlled by plenty of water.

The Rs values of PEDOT:PSS films heat treated at 170℃ are lower than those of PEDOT:PSS films heat-treated at 120℃. There was little difference in the decrease of Rs values by the heat-treatment between pristine PEDOT:PSS and monool-added PEDOT:PSS films, which implies that decrease of the Rs values are possibly caused not by the monools, but by the instability of the nano-structure of PEDOT:PSS molecules

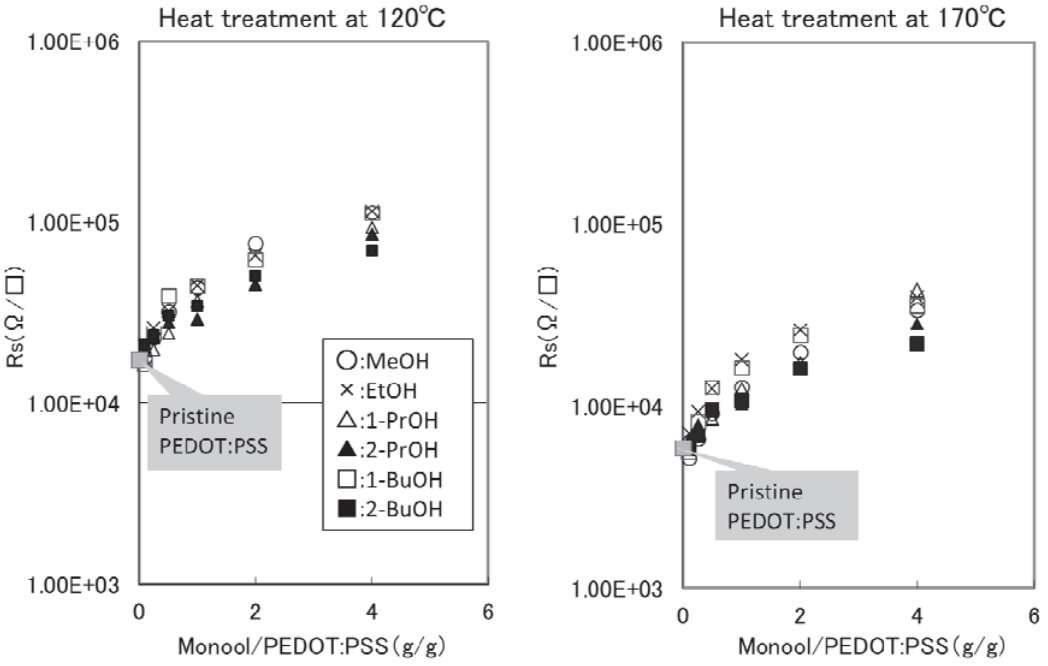


**FIGURE 1.** Effect of monools on the conductivity of PEDOT:PSS films

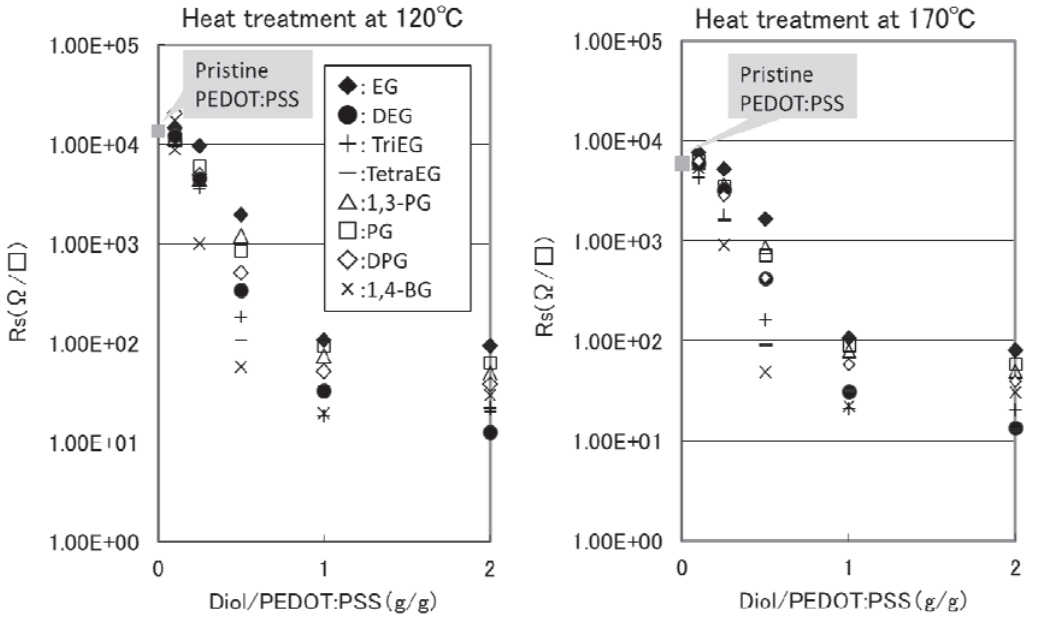


**FIGURE 2.** Effect of diols on the conductivity of PEDOT:PSS films

## Addition effect of diols on the conductivity of PEDOT:PSS films

The addition effect of diols on the Rs values of PEDOT:PSS films was shown in Fig.2. Rs values of PEDOT:PSS films decreased with the addition of diols, and there is a large difference in the conductivity enhancement effect among the species of diols. 1,4-BD showed the highest conductivity enhancement effect among the diols. Its addition effect was higher than that of EG, which is commonly used as a second dopant.

There was no change of the Rs values between PEDOT:PSS films heat-treated at 120°C and that heat-treated at 170°C, while that of pristine PEDOT:PSS film is decreased. This suggests the nano-structure in the PEDOT:PSS films prepared from the mixtures of PEDOT:PSS aqueous solution and diols was not changed by the heat-treatment at 170°C. This heat-treatment effect in diol system is much different from that in the monool system. Since b.p. of diols is higher than that of water, water is expected to be evaporated from PEDOT:PSS from the original coating mixture of PEDOT:PSS aqueous solution and diol by the heat-treatment at 120°C, resulting in the condensation of diols, and the formation of PEDOT:PSS/diol mixture solid film. Then diols play a role of the second dopant to decrease the Rs values of PEDOT:PSS. Since the nano-structure was fixed by diols, there was no change of the Rs values of PEDOT:PSS films in spite of heat-treatment at the higher temperature of 170°C.

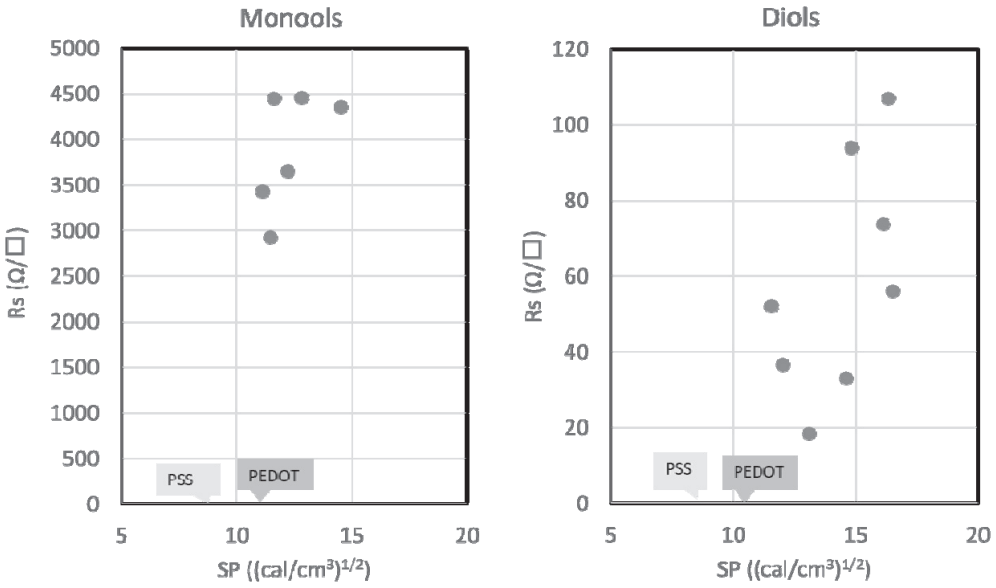


**FIGURE 3.** Relationship between SP values of monools and diols and Rs values of PEDOT:PSS films at the monools & diols/PEDOT wt. ratio of 0.50

## Mechanism for the addition effect of monools and diols on the conductivity of PEDOT:PSS

*Relationship between SP values of monools and diols on the conductivity of PEDOT:PSS films*

Fig.3 shows the relationships between SP values of monools and diols and Rs values of PEDOT:PSS films treated with monools or diols of which weight ratio to PEDOT:PSS is 0.50. It can be seen that monools with a lower SP value give rise to PEDOT:PSS film with a little lower resistivity, but the Rs values of PEDOT:PSS films have little dependence on their SP values. The study of diols showed a dependence of Rs values of PEDOT:PSS films on their SP values, while there was little dependence of Rs value on the SP values with monools. Diols with SP values close to around 10 produced PEDOT:PSS films with lower resistivity. The difference in the addition effect is related to the boiling point of monools and diols. Thinking of the process of PEDOT:PSS film formation from the aqueous PEDOT:PSS solution with monools with a lower boiling temperature than water, monools are removed from the aqueous PEDOT:PSS coating layer faster than water at the solidification temperature of around 100°C. Then there is

some possibility that monools added in PEDOT:PSS aqueous coating solution have little influence on the conductivity enhancement. On the other hand, diols have an effect on the conductivity of PEDOT:PSS films, since their boiling points are larger than water. On the solidification of PEDOT:PSS aqueous coating layer, water is removed faster than diols to leave PEDOT:PSS/diols mixture without water. So Rs values of PEDOT:PSS films added with diols were dependent on the SP values of diols as shown in Fig.3.

*Mechanism for the conductivity enhancement of PEDOT:PSS by diols as a second dopant*

The SP values of PEDOT and PSS are 10.4 and 8.4 respectively[8,9]. The PS value of PEDOT:PSS (PEDOT doped with PSS) is expected to be larger than those of PEDOT and PSS, since PEDOT:PSS is a kind of salt and more ionic. Diols with the SP values ranging from 12 to 14 exhibited higher conductivity enhancement effect. Such SP values are expected to be close to that of PEDOT:PSS. AS for the mechanism of second dopant effect by diols, PEDOT:PSS molecules are easily solvated with diols, which brings about the dissolution of PEDOT or PSS and removal of PSS from PEDOT:PSS. Consequently, the rise of PEDOT/PSS ratio leads the orientation and crystallization of PEDOT molecules, resulting in the conductivity enhancement of PEDOT:PSS films.

## CONCLUSION

The study of the addition effect of aliphatic monools and diols on the conductivity of PEDOT:PSS disclosed that
1)there is a large difference in conductivity enhancement effect between monools and diols,
2)the addition of monools have no effect on the conductivity enhancement of PEDOT:PSS films,
3) the addition of diols enhanced the conductivity of PEDOT:PSS films and their conductivity enhancement degree were dependent on the species (chemical structure) of diols, where 1,4-BD showed the highest conductivity enhancement effect,
4)there is good relationship between the SP values of diols and their conductivity enhancement ability, and the diols with the SP values close to PEDOT (10.4) have higher conductivity enhancement ability,
5)diol addition effect was attributable to its good solubility to PEDOT:PSS molecules.



## ACKNOWLEDGMENTS

This work was partly supported by JSPS KAKENHI (Grant Number 25420727) and Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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